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Thermal Properties of Spider's Thread

Shigeyoshi Osaki[1)]

大崎　茂芳[1)]：クモの糸の熱的性質

Abstract : Thermal properties of drag lines collected from *Nephila clavata*, *Yaginumia sia* and *Argiope amoena* were studied by differential scanning calorimetry (DSC) and thermogravimetry (TG) at temperatures from 20°C to 600°C. The DSC thermograms obtained for *N. clavata* showed an endothermic peak at ca. 100°C and exothermic peaks at ca. 300, 340, 500 and 580°C. The former could be ascribed to the desorption of water from the protein constituting drag lines and the latter to decomposition of the protein. Tce spider's silk thread was stable even above 200°C but completely decomposed at ca. 600°C. The thermal properties of drag lines were found to change with season and depended on the sex as well as species of the spider. Such difference in the thermal properties may be ascribed to the differences not only in the physical properties such as the morphology of silks, the molecular weight and density but also in the chemical structure such as the amino acid composition.

Introduction

All spiders produce silk thread (Foelix, 1982), and about half kinds of them build orb-webs consisting of several kinds of silk thread such as the frame, radial and sticky spiral thread (Jackson, 1971; Osaki, 1985; Yaginuma, 1986). Generally, spiders spin orb-webs at temperatures between 10°C and 50°C. The attachment silk thread stuck on some objects such as rocks or metal fences should be heat-stable even at high temperatures between 60°C and 100°C.

It is meaningful to study the thermal properties of spiders' silk thread from the heat-resistant point of view. However, the thermal properties have not as yet been studied, probably because of a difficulty in collecting drag lines, while spider threads have been studied mainly from morphological and mechanical points of view (Jackson 1971, Denny, 1976; Work, 1976, 1981; Robinson, 1978; Foelix, 1982; Work & Morosoff, 1982). Recently, the author developed an instrument to overcome this difficulty, and investigated changes in color of spider's thread with season (Osaki, 1985). The present paper deals with the thermal properties of spider's silk in the temperature of 20°C to 600°C and then a comparison with the amino acid composition of the silk.

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1) R&D, Kanzaki Paper Mfg. Co., Ltd., Amagasaki, Hyogo, 660 JAPAN
神崎製紙（株）技術開発本部

Meterial and Method

The silk threads used in the present study were drag lines of *Nephila clavata* L. KOCH 1878, *Yaginumia sia* (STRAND, 1906) and *Argiope amoena* L. KOCH 1878. Many drag lines were obtained by means of the instrument developed by the author. They were forcedly pulled out the bodies of many spiders at a rate of about 20 cm/sec. *N. clavata* and *Y. sia* were collected from the suburb of Takarazuka City in Hyogo Prefecture (Japan) from May to November, while *A. amoena* were collected from Kochi Prefecture (Japan) in August. The weight of female *N. clavata* increases from juvenile in spring to mature sprider in autumn while that of male does not increase appreciably even in autumn. For studying thermal properties of drag lines, differential scanning calorimetry (DSC) and thermogravimetry (TG) were carried out in air at heating rate of 20°C/min by use of micro TG-DSC Thermoflex 8100 manufactured by Rigaku Electric Co., Ltd. The DSC relates to the measurement of change in the amount of heat by automatically compensating the amount of heat so that the temperature of sample should be always kept equal to that of standard sample. The TG also relates to the measurement of change in weight of sample by use of thermobalance. The amino acid analysis was carried out by means of Hitachi high speed Amino Acid Analyzer (835-50 type), Before the amino acid analysis, the silk sample was purified with water containing Triton X100.

The average densities of drag lines at 20°C were determined by flotation method with a mixture of benzene and chloroform: 1.13g/cm^3 for juvenile *N. clavata* in July, 1.29g/cm^3 for mature female *N. clavata* in October, 1.27g/cm^3 for female *Y. sia* in September and 1.28g/cm^3 for female *A. amoena* in August.

Results and Discussion

Figure 1 shows DSC and TG thermograms in the temperature range of 20°C to 200°C for the drag lines of female *N. clavata* collected in October. The endothermic peak observed

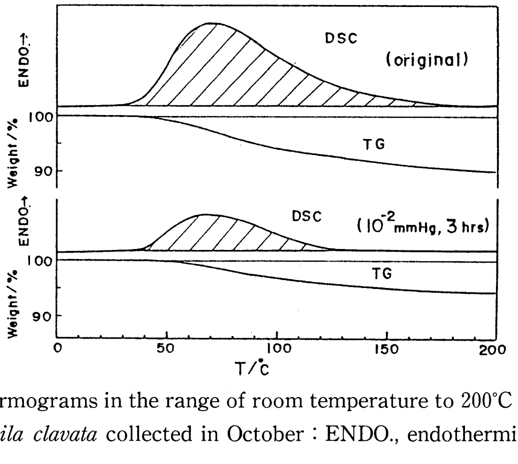

Fig. 1 DSC and TG thermograms in the range of room temperature to 200°C for drag lines forcedly pulled from female *Nephila clavata* collected in October : ENDO., endothermic; T, temperature.

at about 100°C disappeared in the second run after cooling down to room temperature from 200°C. This peak was also found to reduce in height after decompressing at 10^{-2} mmHg pressure for 3 hrs at room temperature. These suggest that the peak may be due to desorption of water molecules adsorbed on silk fibers. The adsorbed water was estimated to be about 10% of the total weight of the sample from the TG curve (20°C-200°C). The broadness of this endothermic peak reflects the distribution of adsorption sites of water molecules.

Figure 2 also shows the DSC and TG thermograms in the range up to 600°C for drag lines of female *N. clavata* collected in October. The color of the drag lines changed to deep yellow at about 200°C and to black at about 400°C, suggesting that the drag lines began to decompose above 200°C. Exothermic peaks can be observed at about 300°C, 340°C, 500°C and 600°C. The first three may be due to degradation of macromolecular proteins, while the last may be ascribed to the evaporation of all the chemical species.

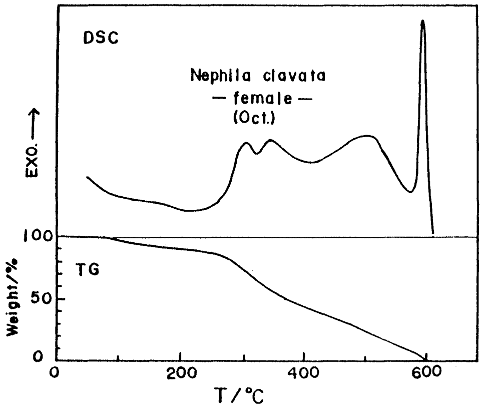

Fig. 2 DSC and TG thermograms in the range of room temperature to 600°C for drag lines forcedly pulled from female *Nephila clavata* collected in October : EXO., exothermic: T, temperature.

These consideration may be supported from the TG curve of Fig. 2. The weight of the sample decreased remarkably with increasing temperature above 200°C and reached about 40% of the initial weight at about 400°C. At 600°C, all the drag lines were completely degraded and their weight approached zero. These findings indicate that the spider's drag lines are thermally stable at least up to 200°C and do not show any melting point.

Figure 3 shows the DSC thermograms for drag lines of female *N. clavata* collected at different seasons. The exothermic peaks appearing above 280°C shift to higher temperature as the *N. clavata* spider grows and the density of her drag lines increases with season. This suggests that the chemical component of drag line proteins may change with season.

In order to make clear the change in the thermal properties of spider's drag lines with season, the sex and the species, the author studied the amino acid composition of drag lines

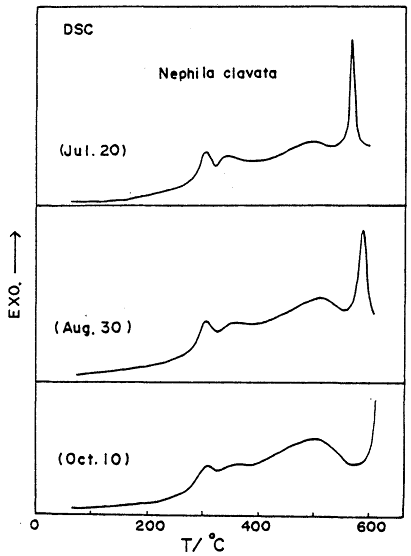

Fig. 3 DSC thermograms for drag lines from female *Nephila clavata* collected at different stages of growing. The densities were determined to be $1.13 g/cm^3$ in July and to be $1.29 g/cm^3$ in October : EXO., exothermic; T, temperature.

consisting of proteins. Table 1 shows the amino acid composition of drag lines at different seasons. The major constituents of the amino acid are glycine (Gly), alanine (Ala), glutamic acid (Glu) and proline (Pro) residues. This means that the macromolecular protein constituting drag lines is made of the repeat of four major amino acids. Apparently, the amino acid composition changes with season. For example, the fraction of polar tyrosine (Tyr) residues in the drag lines of *N. clavata* increases from 0.53 wt% in spring to 3.86 wt% in autumn, while that of proline decreases from 6.32 wt% to 3.35 wt%. The proline fraction of male *N. clavata* in autumn is smaller than that for female *N. clavata* in the same season. The DSC and TG thermograms taken for the drag lines of *N. clavata* in autumn are also shown in Fig.4, The thermal degradation of the drag lines of male *N.clavata* occured at temperatures lower than that for female one (see Fig.2). This difference may come from the difference in the chemical structure ascribed to amino acid composition.

The DSC and TG thermograms for drag lines from three kinds of species are shown in Fig.5. The patterns differ remarkably for the different species which secrete the proteins with different amino acid composition (see Table 1). For example, the fractions of valine (Val) and phenylalanine (Phe) residues for *A. amoena* are larger than those for the other spiders, but the alanine (Ala) fraction is smaller. The fractions of serine (Ser) for *A. amoena* and *Y. sia* are much larger than those for *N. clavata*. In this way, the difference in the thermal behavior among these spiders may also come from the difference in the chemical structure ascribed to amino acid composition.

Table 1 The amino acid composition(wt%) of drag lines collected from *Nephila clavata, Argiope amoena* and *Yaginumia sia.*

Amino acid	*Nephila clavata*					*Argiope amoena* (female)	*Yaginumia sia* (female)
	(female)				(male)		
	May6	Jul.15	Sept.1	Oct.11	Oct.1	Jun.11	Oct.10
Asp	2.33	1.74	1.52	1.45	1.92	4.05	2.37
Thr	1.04	0.86	0.91	0.97	1.09	4.01	1.68
Ser	4.67	3.82	3.69	3.60	3.68	11.72	13.73
Glu	10.06	9.95	9.72	9.24	9.31	8.31	6.65
Gly	38.50	40.73	40.57	40.05	41.98	28.60	37.09
Ala	27.46	28.25	28.17	29.88	30.47	19.69	23.18
Cys	0.16	0.30	0.28	0.22	0.47	0.31	0.43
Val	1.31	1.08	1.11	1.15	1.25	4.13	1.75
Met	0.16	0.08	0.27	0.17	0.09	0.08	0.32
Ile	0.74	0.56	0.54	0.56	0.66	1.93	0.97
Leu	2.97	3.18	3.16	3.02	3.32	4.68	2.09
Tyr	0.53	2.88	3.69	3.86	2.66	3.04	4.43
Phe	0.63	0.43	0.41	0.40	0.52	1.81	0.58
Lys	0.44	0.32	0.29	0.28	——	0.36	0.41
His	0.40	0.09	——	0.08	——	0.12	0.12
Arg	1.79	1.65	1.62	1.73	——	2.11	1.19
Pro	6.32	4.07	4.04	3.35	2.57	5.07	6.85

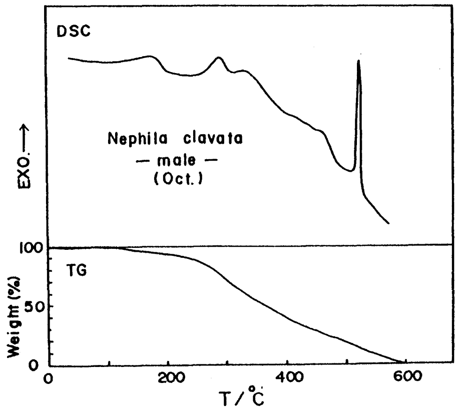

Fig. 4 DSC and TG thermograms for drag lines from male *Nephila clavata* collcted in October : EXO., exothermic ; T, temperature.

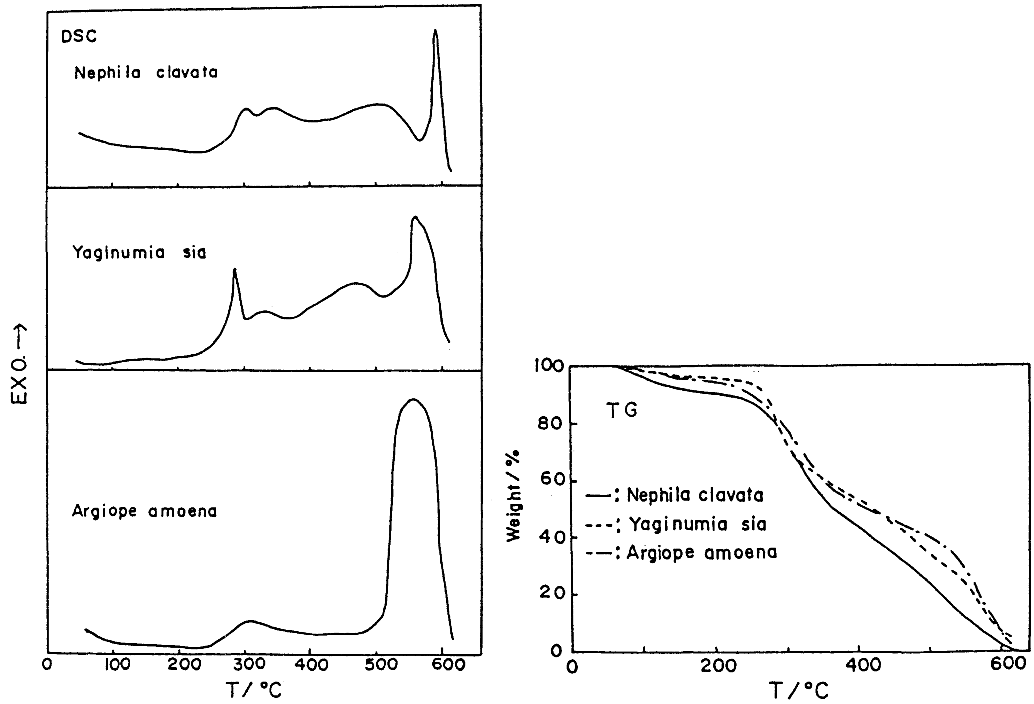

Fig. 5 DSC and TG thermograms for drag lines from three kinds of species *Nephila clavata, Yaginumia sia* and *Argiope amoena* : EXO., exothermic ; T, temperature.

Thus, the differences in the thermal behavior among the season, sex and species may be ascribed to the difference not only in the physical properties such as the morphology of silks, the molecular weight and the crystallinity determined from density but also in the chemical structure such as the amino acid composition.

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摘　要

ジョロウグモ，ズグロオニグモ，コガネグモから採取した牽引糸の熱的性質を，示差走基熱量てんびん(DSC-TC同時測定装置)を用いて，20°Cから600°Cの間で調べた。ジョロウグモの牽引糸では，100℃付近に吸熱ピークが，300℃，340℃，500℃，580℃付近に発熱ピークが観測された。前者のピークは，牽引糸を構成しているタンパク質からの水の脱着に起因し，後者はタンパク質の分解に起因することが推定される。クモの糸は，少なくとも200℃

までは安定であるが，600℃で完全に分解してしまうことがわかった。牽引糸の熱的性質は季節とともに変化し，クモの種のみならず，性に依存することがわかった。熱的性質における差異は，糸の形態，分子量，密度のみならずアミノ酸組成のような化学構造の差異に起因することが考えられよう。

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